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## STRUCTURE OF SHORT-RANGE ORDER IN PHOSPHORUS OXIDE DOPED SILICATE GLASSES

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The structure of short- and medium-range order of silicate glass containing additions of phosphorus oxide is simulated on a computer. The phosphorus atoms can be in oxygen tetrahedra with different symmetry as well as in pentahedra and trigonal bipyramids. Calculations of the P – O bond lengths and the azimuthal angles in the phosphate glass-forming polyhedral are performed and a conclusion is drawn concerning the most likely structural position of phosphorus. The shortcomings of purely ionic models are noted.

**Key words:** silicate glass, phosphate doping, computer models, phosphorus – oxygen polyhedral, bond length, azimuthal angle.

One trend in the modern glass industry is a transition to high-calcium compositions with low magnesium oxide content, making it possible to form glass articles rapidly. While having indisputable economic and technological advantages, such a transition creates problems due to an increase in the crystallization capacity of the melt and decrease of the chemical stability and mechanical strength of the articles. This problem can be solved by introducing small amounts of additives, specifically,  $B_2O_3$  and  $P_2O_5$  [1, 2]. In a previous work [3] we introduced  $P_2O_5$  into commercial silicate glass, i.e., doping the silicate matrix with phosphorus, which gives definite technological advantages.

The effect of phosphorus oxide additives on the short- and medium-range order of the silicate melts and glasses, i.e., at the nanoscale level, can be substantial and has not been adequately studied thus far. This is due to, first and foremost, the complicated character of the interaction of  $P_2O_5$  with the main glass former  $SiO_2$ , as well as with  $Al_2O_3$  and the network modifiers. Here phosphorus can become incorporated into the silicate framework or form phase micro-nonuniformities, which is reflected differently on the properties of glass.

We studied the structural characteristics of the short- and medium-range order in multicomponent silicate glasses containing additions of phosphorus oxide. This investigation is based on computer simulation.

The most commonly used models of glass are based on molecular dynamics and Monte Carlo methods. However,

the conventional schemes of these methods are too inaccurate, even for  $SiO_2$  and  $B_2O_3$  based glasses, because the specific natures of the bridge and terminal oxygen atoms are neglected. The possibility of modeling  $P_2O_5$ -based glass is even more problematic. This is because there are three bridge oxygen atoms in the  $[PO_4]$  tetrahedra and the fourth is bound by a double bond to the central phosphorus atom. Such a structure cannot be described by the universal P – O interaction potential.

According to the information presented in [4], when modifying additives are introduced into phosphate glass the number of double bonds decreases. This can occur as a result of symmetrization of the  $[PO_4]$  tetrahedra. The MPDP method (modified method of neglecting differential overlap) used by B. S. Vorontsov [5] made it possible to obtain the computed values of the bond lengths P – O and P = O as well as the azimuthal angles, which are all in good agreement with the experimental data [6] and nonempirical calculations [7]. The change of the optimal geometry and the equalization of the phosphorus – oxygen bond are confirmed on the basis of these models.

Modeling phosphate systems by means of molecular dynamics on the basis of data from low-angle x-ray diffraction using the Born – Mayer potential and ion charge + 5 and – 2 [8] does not make it possible to obtain a predominately tetrahedral coordination of phosphorus. A substantial number of the  $P^{5+}$  ions are at the center of five-vertex bipyramids, which are interconnected via common vertices, the P – O – P angles being close to the Si – O – Si angles in silica.

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TABLE 1.

Type of polyhedron	Bond length, Å	Bond angle, ...°
Tetrahedron with phosphoryl bond	O = P –	O = P – O –
	1.60282	106.7640
	– O – P –	110.8760
	1.68206	– O – P – O –
	1.68264	110.2510
Tetrahedron with equivalent bonds	1.68677	108.9580
	1.68764	107.6550
	1.68695	109.6330
	1.68420	111.8240
	1.69287	108.1070
Trigonal bipyramid	1.98432	82.3927
	1.83254	100.7540
	1.95308	69.1280
	1.72995	123.3730
	1.80998	70.4437
Pentahedron	Pyramid base	
	1.75649	85.0164
	1.75500	81.3462
	1.75828	101.9050
	1.75134	86.4281
	Vertex	
	1.74821	106.2360
	–	94.1046
	–	87.8930
	–	109.1110

We have constructed a model of glasses in the system  $\text{SiO}_2 - \text{P}_2\text{O}_5 - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O}$  using the Giperkhem-7 program in the ionic-bond variant, which makes it possible to obtain better matching with the previously established structural characteristics. It should be noted that the applicability of the ionic model to phosphate glass cannot be viewed as completely justified. The Pauling electronegativities of the O and P atoms are 3.5 and 2.1, and for the difference of 1.4 the ionicity of the P – O bond is only 39%. This is appreciably lower than in silica (51%).

Our model allows phosphorus to be in an oxygen environment of different symmetry. For phosphorus several different variants of the short-range oxygen environment were considered: for coordination number 4 — a tetrahedron with a double (phosphoryl) bond and tetrahedron with equal bonds tied with a  $[\text{AlO}_4]$  tetrahedron and for CN = 5 — pentahedron and trigonal biopyramid.

Minimization of the geometry shifted the atoms from their initial positions. All optimized phosphate glass-forming polyhedral differ by the degree of departure from symmetry. The main parameters of the topological models of phosphate glass-forming polyhedral are presented in Table 1.

It follows from the data in Table 1 that here the difference between the P = O (1.6 Å) and P – O (1.68 Å) bond

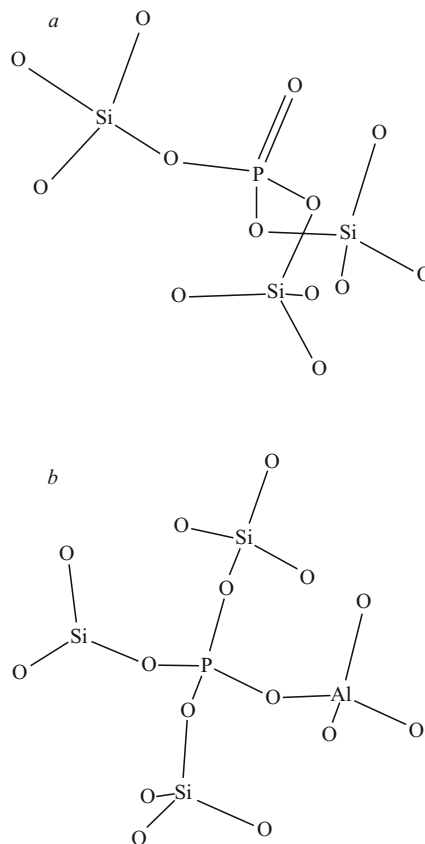


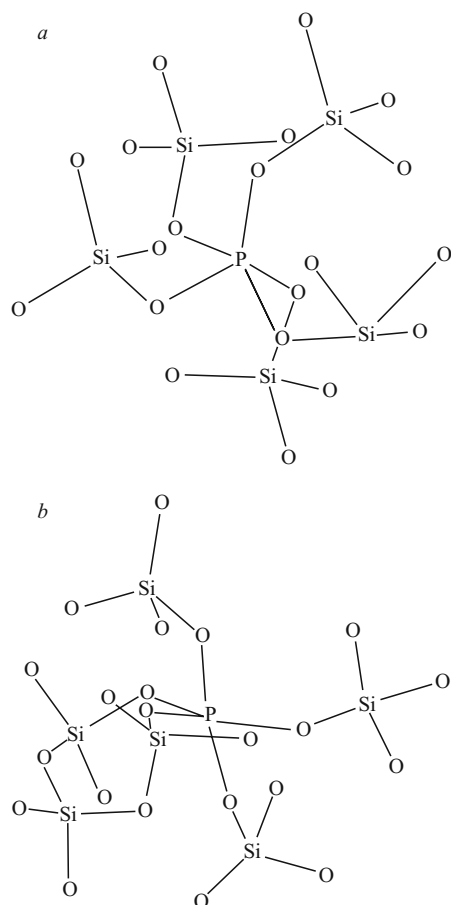
Fig. 1. Structural fragments of silicate glass, containing quadruply coordinated phosphorus with double (a) and equivalent (b) bonds.

lengths is appreciable, though this difference is much smaller than in pure  $\text{P}_2\text{O}_5$  (according to [4], 1.57 and 1.67 Å, respectively). This attests to structural symmetrization of orthophosphate tetrahedra when modifiers are present in the glass. Figure 1 shows the structure of short-range order around an orthophosphate tetrahedron with double phosphoryl and with equivalent bonds.

As result of the presence of uncompensated positive charge on the tetrahedron (Fig. 1b) its position is stabilized if  $\text{Al}_2\text{O}_3$  is present and ties can be formed with  $[\text{AlO}_4]$  tetrahedron, carrying a negative charge. Here the parameters of the bonds and the azimuthal angles different negligibly as compared with the parameters of the single bonds in a tetrahedron with a double bond.

It is evident that in the short-range order structure around pentacoordinated phosphorus, present in the form of a pentahedron, the P – O bond lengths are shorter and this structural polyhedron is more symmetric than a trigonal bipyramid. For pentacoordinated phosphorus located at the center of a trigonal bipyramid it should be noted that the P – O bonds are systematically longer and the symmetry of the structural polyhedron is lower.

Assessing as a whole the results of the construction of topological models describing the structural position of phosphorus in silicate glasses with high content of modifiers



**Fig. 2.** Structure of short-range order around pentacoordinated phosphorus in the form of a pentahedron (a) and trigonal bipyramid (b).

it is evident that such models can be realized, though with different degrees of likelihood. Since glass is amorphous and has a strongly nonequilibrium structure, which forms during

cooling of viscoelastic melt, the structure of the nearest environment of phosphorus can differ substantially from similar structures in crystalline compounds. On the basis of energy considerations, structures with shorter bond lengths, i.e., tetrahedra, are more likely to be formed. It is less likely to find phosphorus in oxygen polyhedra, where its coordination number  $CN = 5$ . The formation of pentahedra is preferable.

It should be noted that models employing ion charges  $+5$  and  $-2$  cannot be accurate for such complex objects as multicomponent silicate glasses doped with phosphorus. It would be more promising to construct models in an ionic-covalent variant. The introduction of a mixed bond makes it possible to improve the correspondence between the empirical data on the properties and the structural characteristics.

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